



Effect of Various Carbonization Processes in the Preparation of Nanoporous Carbon Materials using *Albizia amara* Pod Shell Waste for the Removal of Dyes from Textile Industrial Effluents

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Abstract

Nanoporous activated carbon materials were prepared from abundantly available *Albizia amara* pod shell waste. A series of five nanoporous carbon samples were prepared by subjecting the carbon material to various chemical processes. The physico-chemical properties and adsorption capacities were compared. These materials accumulate superior properties and good adsorption behaviours. The adsorption capacity of selected derived carbon samples using *Albizia amara* pod shell waste prepared by Dolomite process was much greater than the capacities of the other carbons prepared by various processes viz., Acid process, ZnCl_2 process, Sulphate process and Carbonate process. The dye removal from textile industrial effluents by nanoporous carbon adsorption is mainly due to the surface action between the anionic or cationic nature of the dye and the acidic or basic functional groups present on the surface of the carbon material, its isoelectric point (pH_{zpc}), surface area, iodine number etc. This concept of surface action has been widely recognized and the effective usage of the carbon adsorbent has shown new dimensions in studying the adsorption characteristics. The influence of surface area and porosity of the carbon samples on dye removal was analysed. The use of surface modified and chemically treated activated carbons derived from the stem wastes of *Ipomoea carnea* was extensively studied in the removal of dyes. The effects and influence of pK_a values of dyes and isoelectric point (pH_{zpc}) of nanoporous carbon materials were broadly studied and interpreted with dye adsorption onto nanoporous carbon material. The results reveal that the prepared activated carbon could be employed as a low cost alternative for removing toxic and carcinogenic dyes from the textile industrial waste water.

Keywords: Isoelectric point (pH_{zpc}); Nanoporous activated carbon; pK_a values; Surface area adsorption; Surface chemical groups.

1. INTRODUCTION

Activated carbons having high specific porosity high surface areas and extremely versatile adsorbents of major industrial significance. Activated carbon has been extensively used for the purpose of water purification in portion. In particular, it has been commonly used for the removal of organic dyes from textile waste water. In order to improve the adsorption potential of the raw carbon it is subjected to various suitable chemical treatments. Carbon based sorbents show excellent adsorption properties for a considerable number of synthetic dyes. The presence of very small amounts of dyes in water even less than 1 ppm for some dyes is highly visible and undesirable (Robinson *et al.*

2002). The removal of colour from textile waste water is a major environmental problem and they are the first contaminant to be recognized in water (Banat *et al.* 1996). Coloured water is also objectionable on aesthetic grounds for drinking and agricultural purposes (Karthikeyan *et al.* 2010). Nanoporous carbon materials with larger surface area, micro porous character and chemical nature of their surface have made them potential adsorbents for the removal of dyes from industrial waste water. The adsorptive properties of active carbon for removal of pollutants are well documented (Macias *et al.* 1993).

Many industries such as dyestuff, paper, textile and plastics use dyes in order to colour their products

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and also consume substantial amount of water (Elinge *et al.* 2011). Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies. However, the preparation of carbon sorbents is generally energy consuming. Consequently, the commercially available products are fairly expensive. Since a large amount of carbon sorbent is needed for the removal of dyes from a large volume of effluent, the expenses involved hamper their application (Forgacs *et al.* 2004). Synthetic dyes and pigments are extensively used in dyeing and printing industries. Over ten thousand tons per year and approximately 10000 dyes are produced annually worldwide, of which 10 % is lost in the industrial effluents (Kishore K Das *et al.* 2011). As synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, the adsorption of synthetic dyes on inexpensive and efficient solid supports was considered as a simple and economical method for their removal from wastewater. Adsorption is operative in most natural, physical, biological, and chemical systems and is widely used in industrial applications such as activated charcoal and synthetic resins. Carbons with excellent surface properties and specific functionalities should be developed to create a high affinity for adsorbate adsorption.

The use of carbon based on relatively expensive starting materials is also unjustified for most pollution control applications. Hence, widely available plant sources are utilized to reduce the concentration of dyes from wastewater and industrial effluents. In the present study, the physico-chemical and adsorption characteristics of nanoporous activated carbon derived from *Albizia amara* pod waste have been measured and their capacity to remove commonly used synthetic dyes such as Acid Red 2 (Methyl Red), Basic Violet 10 (Rhodamine B), Reactive Blue 171 and Direct Red 28 (Congo Red) has been evaluated.

2. MATERIALS & METHODS

2.1 Adsorbent

Albizia amara, is a tree in the fabacea family. It includes southern and eastern Africa from South Africa to Sudan and in India and in Sri Lanka. *Albizia amara* is a small moderate sized much branched deciduous tree with smooth dark green scaly bark. Its root system is shallow and spreading fruits are oblong pods about $10^{-28} \times 2^{-5}$ cm. Light brown and thin since tree is abundantly available has no specific significance, it can be utilized as an alternative low-cost adsorbent.

The pod shell of *Albizia amara* were collected from in and around Erode district, TamilNadu, India. They were cut into small pieces and dried in sunlight

until the moisture was evaporated. The dried materials were used for the preparation of activated carbons using physical and chemical activation methods.



Fig. 1: Image of *Albizia amara* pod shell

2.2 Adsorbates

The dyes used for this study were supplied by S.D. Fine chemicals, Mumbai, India and used as such without further purification. The properties and structure of dyes chosen are represented in Table 1 and Table 2 respectively.

Table 1. List of dyes used for Adsorption study

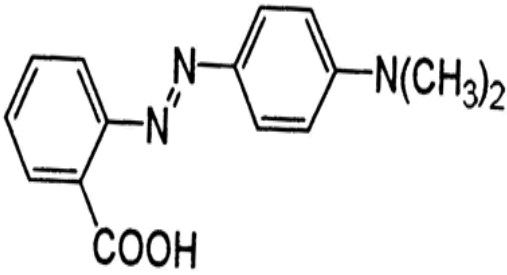
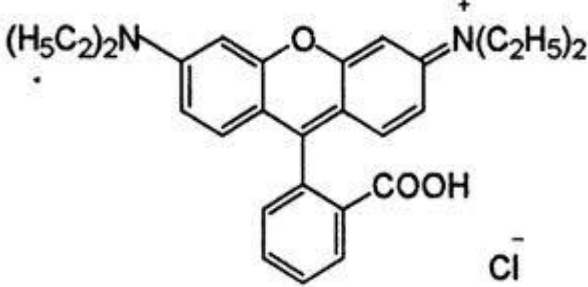
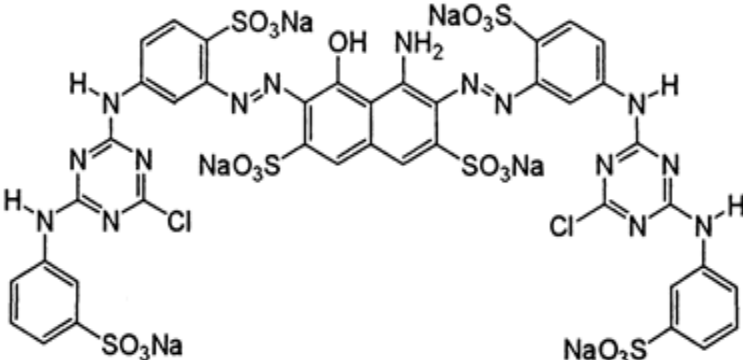
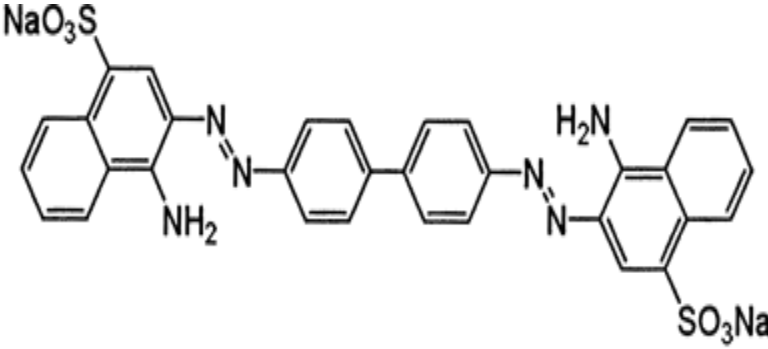
S. No	Class	C.I. No.	C.I. Name	pKa
1	Acid dye	13390	Acid Red 2	5.1
2	Basic dye	42555	Rhodamine B	4.1
3	Reactive dye	18972	Reactive Blue 171	5.2
4	Direct dye	22120	Direct Red 28	4.2

2.3 Carbonization Procedures

Fundamentally there are two different activation methods for the preparation of activated carbon. They are physical and chemical activation methods respectively. The physical activation involves carbonization of precursor followed by activation of the resulting char in the presence of activating agents such as steam or CO₂. But, the chemical activation involves the carbonization of the precursor in the presence of chemical agents.

In the chemical impregnation method, impregnation of precursor is done first with the particular chemical followed by carbonization and activation. Chemical activation is more advantageous than physical activation with respect to higher yield, more surface area and better development of porous structure (Rengaraj *et al.* 1998).

Table 2. Structure of dyes for adsorption study

Name of the Dye	Structure
Acid Red 2	
Rhodamine B	
Reactive Blue 171	
Direct Red 28	

2.3.1 Carbonization with Phosphoric acid

The dried material was treated with excess of Phosphoric acid. Charring of the material occurred immediately with the evolution of fumes and heat. After the reaction subsided, the material was left in air oven at 140-160 °C for a period of 24 hours. The dried masses were washed with excess of water to remove the free acid residues. They were dried at 110 °C, sieved and finally activated at 800 °C (Karthikeyan *et al.* 2008).

2.3.2 Acid process with Sulphuric acid

The dried material was treated with excess of Sulphuric acid. Charring of the material occurred immediately with the evolution of fumes and heat. After the reaction subsided, the materials was left in air oven at 140-160 °C for a period of 24 hours. The dried masses were washed with excess of water to remove the free acid residues. They were dried at 110 °C, sieved and finally activated at 800 °C (Karthikeyan *et al.* 2008).

2.3.3 Carbonate process with Potassium carbonate

The materials to be carbonized were soaked with 10% solution of K_2CO_3 for a period of 24 hours. After impregnation the liquid portion was decanted off and the material was dried. The dried mass was subjected to carbonization process at 400 °C, powdered well and thermally activated at 800 °C for a period of 10 minutes (Karthikeyan *et al.* 2008).

2.3.4 Carbonization with Sodium Sulphate

The materials to be carbonized were soaked with 10% solution of Na_2SO_4 for a period of 24 hours. After impregnation the liquid portion was decanted off and dried at 120 °C. The dried and neutralized mass was subjected to carbonization process at 400 °C, powdered well and thermally activated at 800 °C for a period of 10 minutes (Jambulingam *et al.* 2007).

2.3.5 Carbonization with Zinc chloride

The materials to be carbonized were soaked with 10% solution of $ZnCl_2$ for a period of 24 hours. After impregnation the liquid portions decanted off and dried at 120 °C. The dried and neutralized mass was subjected to carbonization process at 400 °C, powdered well and thermally activated at 800 °C for a period of 10 minutes (Jambulingam *et al.* 2007) and dried at 110 °C for a period of 10 minutes (Karthikeyan *et al.* 2008).

2.4. Characterization of the Activated Carbon

Table 3. List of various activation processes and abbreviation of activated carbon samples

S. No	Activated Carbon Sample	Treatment
1	AAAC1	Acid process using H_3PO_4 impregnation
2	AAAC2	Carbonate process using H_2SO_4 impregnation
3	AAAC3	Chloride process using K_2CO_3 impregnation
4	AAAC4	Sulphate process using Na_2SO_4 impregnation
5	AAAC5	Dolomite process using $ZnCl_2$ impregnation

The materials treated with Concentrated H_2SO_4 , 10% K_2CO_3 , 10%, $ZnCl_2$ 10% and dolomite have been named as AAAC1, AAAC2, AAAC3, AAAC4 and AAAC5 respectively. The particle size of the well powdered carbon materials ranges from 75 to 180 μm . The physico-chemical properties of treated activated carbon were measured by suitable standard methods (Karthikeyan *et al.* 2008). The pH and conductivity were analyzed using Elico make pH meter (LI-120) and conductivity meter (M-180) respectively. Moisture Content (%) by mass, Ash Content (%) by mass, volatile matter (%), fixed carbon (%), Bulk Density (g/L), Specific gravity, Water soluble matter, Acid soluble matter, Iodine number (mg/g), Surface Area (m^2/g), Phenol adsorption capacity and porosity were analyzed as per standard procedures (ISI, 1989). The Isoelectric point or Zero point charge (pH_{zpc}) of the carbon samples were measured by using the pH drift method (Jia *et al.* 2002). A known quantity of a series of ten K_2CO_3 solutions having the initial pH values ranging from 1 to 10 were prepared using dilute HCl and dilute NaOH. All the ten K_2CO_3 Solutions taken in ten different bottles were mixed with 0.5 g of *Albizia amara* Activated Carbon (AAAC) for a specified period of time. Then the solutions were filtered off and the activated carbon was separated. The final pH values of the ten solutions were measured and thereby calculation of ΔpH was made by subtracting the initial pH values from final pH values. The graph was drawn by plotting the final pH values against ΔpH . From the graphs plotted, the pH_{zpc} (point of zero charge) of the Nanoporous activated carbon was determined. Thus, the pH_{zpc} values of AAAC1, AAAC2, AAAC3, AAAC4 and AAAC5 were obtained and shown in table 3. The surface area of activated carbon was measured using BET equations at liquid N_2 temperature using Nova 1000, Quanta chrome analyser.

2.5. Dye Adsorption studies

All reagents used were of AR-grade (E-merk). Different concentrations of individual dye solutions such as Acid Red 2, Direct Red 28, Reactive Blue 171 and Basic Violet 10 were prepared with distilled water. 50 ml of each chosen dye solution of known initial concentration (C_0) and initial pH was taken in a 100 ml screw-cap conical flask with a required amount of adsorbent and was agitated at a speed of 200 rpm in a temperature controlled thermodynamic shaker bath at 30 °C for a specified period of time. Then the solution was filtered through a 0.45 μ m membrane filter. The concentrations of dyes in solutions were determined before and after adsorption using Elico UV-visible spectrophotometer. The amount of dye adsorbed and adsorption efficiency was calculated as follows:

$$\text{Adsorption efficiency (\%)} = ((C_0 - C)/C_0) \times 100$$

where, C_0 = initial dye concentration (mg/l),

C = residual dye concentration (mg/l).

3. RESULTS & DISCUSSION

3.1 Physico-chemical characteristics of Activated Carbon prepared from *Albizia amara* pod shell waste

The physico-chemical parameters of chemically treated nanoporous activated carbon obtained from *Albizia amara* pod shell waste were illustrated in table 4.

The pH of the carbon derived from acid treatment was lower than other carbons impregnated with dolomite, Chloride, Sulphate and Carbonate salts. The higher pH values of AAAC2, AAAC4 and AAAC5 can be related to the introduction of some basic functional groups like carbonate ions and removal of acidic functional groups when compared with the lower pH value of acid treated carbon AAAC1. The results reveal that the dolomite treated and acid treated carbon samples have effectively adsorbed the basic dye. The Conductivity values indicated in table 4 do not show much variation which implies that the carbon samples were almost free from dissolved impurities. The cations in acidic carbon and anions in basic carbon are responsible for these similar conductivity values. It has been found that the pores of the carbon were completely available for the accumulation of adsorbate (Bansal *et al.* 1988; Bansal *et al.* 2002). Low moisture content of carbon indicates that the carbon samples have poor affinity on water. Even though moisture content of the carbon does not affect the adsorptive power, it dilutes the carbon which demands the use of additional weight of carbon during treatment processes

(Bansal *et al.* 1988). The higher moisture content of dolomite treated carbon may be due to the moisture adsorptive nature of carbonate ions present in the activated pores of carbon particle.

The fixed carbon values of the prepared carbon samples obtained by using the values of moisture content, volatile matter and ash content indicate the presence of higher amount of fixed carbon though the ash content value of dolomite treated carbon was slightly higher than the carbons prepared by other activation processes. The ash content of the carbon samples substantiate that dolomite treated carbon has higher inorganic constituent than acid treated carbon. These values of ash content can be attributed to minimum amount of inorganic content and high fixed carbon. The carbon having little amount of ash content may remove the inorganic contaminants effectively (Bansal *et al.* 2002; Pereira *et al.* 2003). The Carbon of higher bulk densities are suitable for treatment processes as the low density carbon suspends on water and the treatment processes cannot be effective. The lower bulk density values of carbons demonstrate that the carbon samples are highly branched and porous with more void space (Summers *et al.* 1988).

Similarly, the lower bulk density values of carbons derived from *Albizia amara* also demonstrate that the carbon samples are highly branched and porous. Carbon prepared from the treatments with dolomite and Na_2SO_4 gives higher water soluble constituents which implies that the presence of water soluble impurities may have impact on the treated water. The values of water soluble matter and acid soluble matter are low in carbon prepared from acid treatment. This depicts that the acid treatment lowers the leachable constituents.

The isoelectric point or zero point charge implies that the prepared carbon is free from surface charges nearby neutral pH. Hence the carbon samples are suitable for the treatment of water even at the neutral medium. The higher level of iodine number reveals that the presence of high porosity in the carbon. The carbon samples AAAC2 and AAAC4 are comparatively having higher porosity which highly influences the adsorption capacity of nanoporous carbon samples. These results are supported by the surface area and phenol adsorption capacity of the carbon samples. Chemically modified activated carbon was found to be an excellent adsorbent for the basic and acidic dyes but direct dye showed less affinity for adsorption (Hirata *et al.* 2002). The usefulness of carbon is a result of their specific surface area. Activated Carbon AAAC2 having larger surface area removed all the four dyes effectively from their aqueous solutions.

Table 4. Physico-Chemical parameters of Activated Carbon from *Albizia amara*

Parameters	AAAC1	AAAC2	AAAC3	AAAC4	AAAC5
pH	5.11	6.34	7.82	7.90	7.62
Conductivity, Ms/cm	0.31	0.37	0.42	0.23	0.42
Moisture Content, %	8.40	6.80	6.60	5.45	7.16
Ash Content, %	7.74	10.06	10.78	11.81	8.64
Bulk Density, g/L	0.50	0.33	0.29	0.23	0.41
Specific Gravity, S	0.83	0.63	0.92	0.93	0.83
Water Soluble Matter, %	0.85	0.54	0.39	0.34	0.82
Acid Soluble Matter, %	0.49	1.65	1.07	0.88	1.53
Zero Point Charge in pH Units	5.7	5.8	5.9	6.0	5.9
Porosity, %	0.27	0.21	0.16	0.13	0.24
Iodine Number, mg/g	521	199	655	428	571
Surface Area, m ² /g	481	393	298	342	407
Phenol Adsorption Capacity, mg/g	3.00	1.20	3.00	3.80	2.60
Volatile matter, %	9.20	18.8	14.8	17.0	11.2
Fixed carbon, %	82.40	72.4	78.6	73.4	80.2
Yield, %	73	45	41	35	57

Effect of surface area and surface chemical groups on the adsorption capacity

Removal of the dye Rhodamine B by prepared activated carbon samples

The effectiveness of removal of the dye Rhodamine B from aqueous solution by various chemically treated Nanoporous carbon samples is

$$\text{AAAC1} > \text{AAAC5} > \text{AAAC2} > \text{AAAC4} > \text{AAAC3}$$

The higher surface area of the H₃PO₄ treated carbon AAAC1 may perhaps be the reason for its greater affinity towards the adsorption of basic dye compared with ZnCl₂ treated carbon AAAC5 which has comparatively lower surface area. The acid treated carbon AAAC2 also has greater adsorption towards the basic dye Rhodamine B due to the presence of acidic functional groups on its surface. The similar adsorptive results of basic dyes like gentMethylene Blue and Gentian Violet by carbonaceous material produced from coffee grounds depended upon the acidic polar groups on the adsorbent material (Hirata *et al.* 2002) also reported. Each low-cost adsorbent has its specific advantage in waste water treatment. For example clay minerals exhibit a strong affinity for basic dye (Bagane *et al.* 2000).

Removal of the dye Direct Red 28 by prepared activated carbon samples

The effectiveness of removal of the dye Direct Red 28 from aqueous solution by various chemically treated nanoporous carbon samples is

$$\text{AAAC1} > \text{AAAC5} > \text{AAAC3} > \text{AAAC2} > \text{AAAC4}$$

The Carbon AAAC1 having higher surface area removed the Direct Red 28 dye from aqueous solutions effectively. The adsorption of dyes is higher on activated carbon having higher value of surface area. The presence of surface polar groups on the adsorbent has greater influence on the adsorptive nature of the carbon (Amit Bhatnagar *et al.* 2006).

The Carbon AAAC2 and AAAC4 having higher surface area but with bulky radicals like sulphate may decrease the adsorptive efficiency. The similar results were also reported by the removal of the dye Direct Congo Red by waste red mud (Namasivayam *et al.* 1998) a by-product of aluminium production with 90 minutes of equilibrium time, rice hull ash (Chou *et al.* 2001) and banana pith (Namasivayam *et al.* 1997).

Removal of the dye Reactive Blue 171 by prepared activated carbon samples

The effectiveness of removal of the dye Reactive Blue 171 from aqueous solution by the various chemically treated nanoporous carbon samples is

$$\text{AAAC1} > \text{AAAC5} > \text{AAAC2} < \text{AAAC4} < \text{AAAC3}$$

The carbon samples AAAC1, AAAC2 and AAAC5 demonstrate greater adsorption of the dye Reactive Blue 171. These three carbon samples have greater affinity towards the removal of the anionic dye Reactive Blue 171. This is due to the presence of acidic functional groups in the voids of carbon AAAC1, AAAC2 and also due to the higher surface area and porosity of carbon AAAC5. Similar investigations reported the effect of modified carbon surface in the

adsorption of three anionic reactive dyes remazol yellow, remazol black and remazol red from its aqueous solutions (Al – Degs *et al.* 2000). The recent reported adsorption capacity values 712.3, 278, 714 of Reactive Red 2 (Chio *et al.* 2001), Reactive Red 5 and Reactive Orange 107 (Aksu *et al.* 2001) respectively with commercially activated carbon materials and adsorption of Reactive Red 120, Reactive Red 141 and Reactive Red 2 (Netpradit *et al.* 2003) with low cost adsorbent yields the adsorption capacity values 48.31, 56.18, 62.5 respectively indicates the substantial removal of reactive dye with chemically modified surfaced carbon.

Removal of the dye Acid Red 2 by prepared activated carbon samples

The effectiveness of removal of the dye Acid Red 2 from aqueous solution by the various chemically treated nanoporous carbon samples is

$$\text{AAAC1} > \text{AAAC2} > \text{AAAC3} > \text{AAAC4} > \text{AAAC5}$$

The carbon AAAC1 and AAAC2 exhibit the larger elimination of the dye Acid Red 2 from the aqueous solution due to their higher surface area and porosity. This is also supported by their iodine number and phenol adsorption capacity.

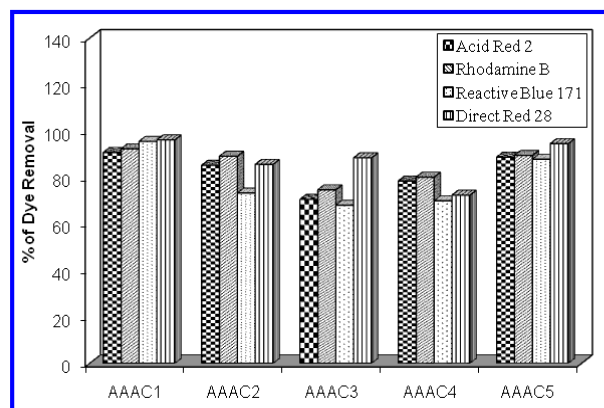


Fig. 2: Dye removal percentage of various activated carbons

Adsorption of acid dye by H_3PO_4 treated carbon AAAC1 having higher surface area reveals the presence of anionic surface groups (carbonate ions) on its surface. This is supported by its pH value. Due to the smaller surface area and lower iodine number of Na_2SO_4 treated carbon AAAC4 shows lower adsorption capacity towards the adsorption of Acid dye. By the use of activated carbon, other components of the waste water can also be adsorbed by the carbon and the competition among the adsorbates can influence the dye binding capacity. The similar results were also reported that the percentage removal of the methyl red by the

acid treated sugarcane baggase carbon was higher due to higher surface area and available adsorbent sites when compared to the formaldehyde treated sugarcane baggase carbon having comparatively lower surface area (Saiful Azhar *et al.* 2005). Fig.2 clearly indicates that the percentage of anionic and cationic dye removal for five different activated carbons prepared from *Albizia amara* pod shell waste.

3.1 Effect of pKa of dyes and pH_{zpc} of adsorbent

Among the prepared carbon samples, AAAC1 (zpc value is 5.7) was chosen to study the adsorption of various dyes. Fig. 3 clearly shows the adsorption of anionic dyes chosen increases when the solution pH is less than the isoelectric point (zpc) of activated carbon as the surface of the carbon becomes more positively charged. Hence, the electrostatic attraction takes place between the anionic dyes and the positively charged sites on the carbon at lower solution pH. The adsorption of cationic dyes chosen increases when the solution pH is greater than the isoelectric point (zpc) of activated carbon as the surface of the carbon becomes more negatively charged. Hence, the electrostatic attraction takes place between the cationic dyes and the negatively charged sites on the carbon at higher pH. The adsorption of anionic dyes such as Acid Red 2 ($\text{pK}_a = 5.1$), Reactive Blue 171 ($\text{pK}_a = 5.7$), Direct Red 28 ($\text{pK}_a = 4.2$) decreases above their pK_a values. The adsorption of cationic dye increases above its pK_a value. The adsorption of the basic dye Rhodamine B ($\text{pK}_a = 4.7$) starts increasing above its pK_a value. At a pH of solution above the pH_{zpc} of the adsorbent, the surface of adsorbent is negatively charged and can attract cations from the solution and when solution $\text{pH} < \text{pH}_{\text{zpc}}$, the surface of adsorbent is positively charged and attractive to anions (Sharma *et al.* 2009; Sun *et al.* 2007).

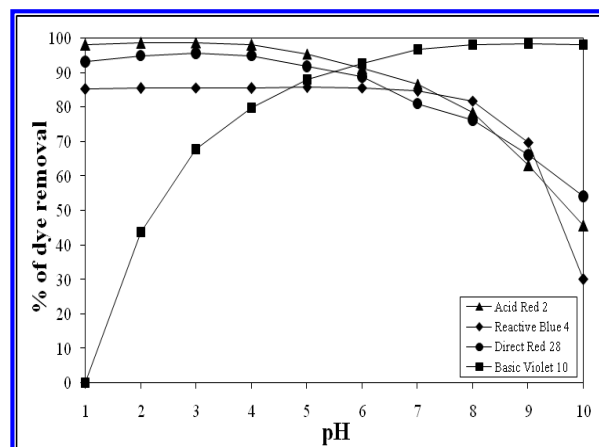


Fig. 3: Effect of pKa of dyes and pH_{zpc} of adsorbent on dye removal

3.2 Scanning Electron Micrograph studies

The morphology of the surface of the prepared Nanoporous activated carbon samples was examined using Scanning Electron Micrographs. These micrographs provide positive reception of the porosity of adsorbents and consequently a qualitative evaluation of their ability to adsorb the dye molecules in solution.

AAAC1, AAAC2 and AAAC5 have many pores, small cavities and rough areas with micro pores which were clearly found on the surface. This shows that H_3PO_4 , H_2SO_4 and ZnCl_2 were effective to create well developed pores with uniform distribution on the surface of the precursor, therefore leading to the activated carbon with large surface area and porous structure.

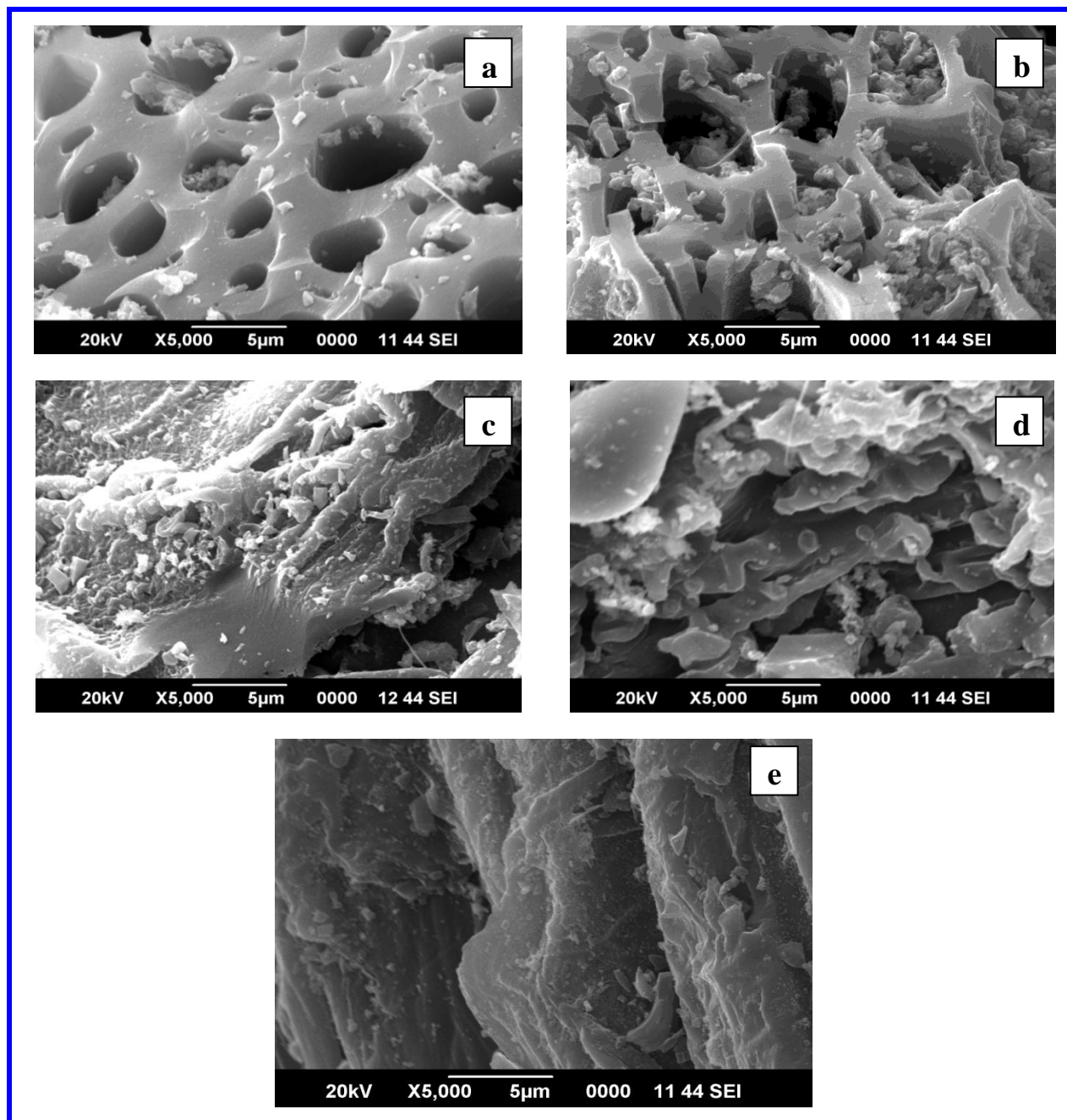


Fig. 4: SEM images of *Albizia amara* pod shell activated carbons prepared from various process
 (a) H_3PO_4 process (b) H_2SO_4 process (c) K_2CO_3 process (d) Na_2SO_4 process (e) ZnCl_2 process

3.3 FTIR Study

The FTIR spectra were recorded on pellets obtained by pressing mixture of 1 mg of the adsorbent and 100 mg of dried KB ruder pressure. The FTIR spectrum of adsorbents prepared from various process show weak and broad peaks in the region of 500-4000 cm^{-1} . The bands appears around 1035 cm^{-1} for the chosen adsorbents indicating C-O stretching C-O-C group in carboxylic and alcoholic group (Wang *et al.* 2011). An IR spectrum consists of two regions:

(i) There are absorption bands above 1500 cm^{-1} that can be assigned to individual functional groups, whereas (ii) the region below 1500 cm^{-1} (the finger print region) contains many bands within the fingerprint region, which arise from functional groups, can be used for identification, but such assignments should be considered only an aid to identification and not as conclusive proof (Hesse *et al.* 1997). The peaks appears around 1450 cm^{-1} in AAAC1, AAAC2, AAAC3 and AAAC4 are due to the -OH stretching and bending vibration originating in the molecule.

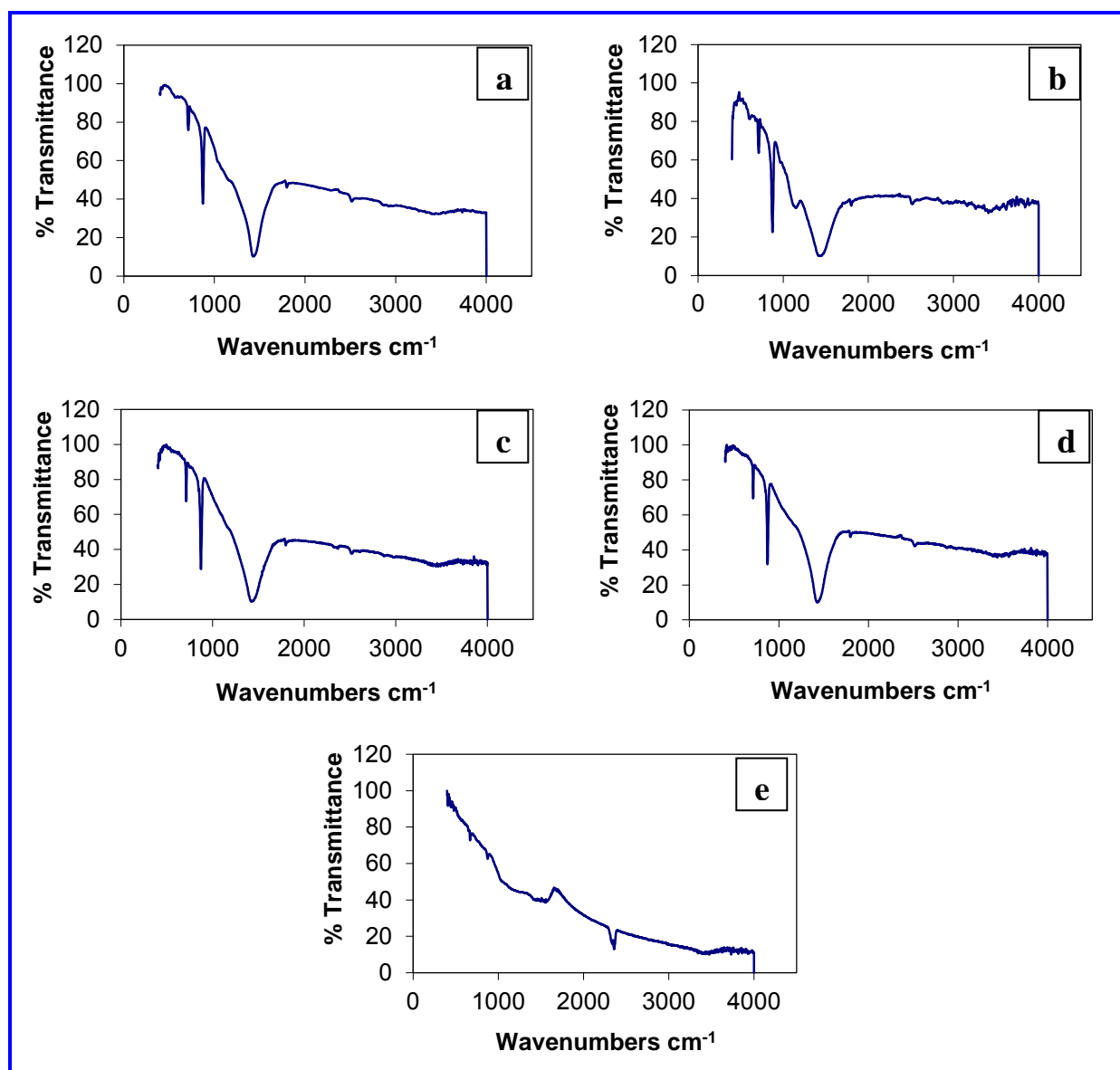


Fig. 5: FTIR images of *Albizia amara* pod shell activated carbons (a) AAAC1 (b) AAAC2 (c) AAAC3 (d) AAAC4 (e) AAAC5

4. CONCLUSION

From the results of the present investigation, we can conclude that

1. Nanoporous activated carbons can be prepared conveniently and economically from *Albizia amara* plant source which is abundantly present.
2. The prepared adsorbents have a substantial variation in the dye removal capacity. The adsorption capacity of carbon sample prepared by H_3PO_4 process was much greater than the capacities of the other carbons prepared by various processes.
3. These carbon samples significantly remove the dyes from aqueous solutions based on their physico-chemical properties.
4. The extensive characterization studies of the different activated carbons prepared by various processes reveal that the carbons obtained from *Albizia amara* pod shell waste can be assessed as superior grade carbon for adsorption processes.
5. Activated carbon with good surface properties from various treatment procedures were identified. The surface chemical groups of the activated Carbon play a vital role in removing variety of dyes from its aqueous solutions.
6. H_3PO_4 and Na_2SO_4 treated activated carbons have very high surface area and porosity.
7. Porosity plays a vital role in determining the adsorption capacity of carbons.
8. The adsorption of anionic dyes increases when the solution P^H is less than the isoelectric point (zpc) of activated carbon as the surface of the carbon becomes more positively charged.
9. The adsorption of cationic dyes increases when the solution pH is greater than the isoelectric point (zpc) of activated carbon as the surface of the carbon becomes more negatively charged.
10. The adsorption of anionic dyes decreases above their pKa values.
11. The adsorption of cationic dyes increases above their pKa values.

REFERENCES

- Aksu, Z., Tezer, S., Biosorption of reactive dyes on the green alga *Chlorella vulgaris*, *Proc Biochem.*, 40(3-4), 1347-1361(2005).
doi:10.1016/j.procbio.2004.06.007
- Al-Degs, Y., Kharaisheh, M. A. M., Allen, S. J., Ahmad, M. N., Elimination d'un colorant des effluents de l'industrie textile par adsorption, *Wat. Res.*, 34, 927(2000).
doi:10.1016/S0043-1354(99)00200-6
- Amit Bhatnagar, Minocha, A. K., Conventional and non-conventional adsorbents for removal of pollutants from water — A review, *Indian J. Chem. Technol.*, 13, 203(2006).
- Bagane, M., Guiza, S., Elimination d'un colorant des effluents de l'industrie textile par adsorption, *Ann. Chim. Sci.Matter.*, 25, 615(2000).
doi:10.1016/S0151-9107(00)90003-5
- Banat, I. M., Nigam, P., Singh, D., Marchant, R., Microbial decolorization of textile-dyecontaining effluents: A review, *Bioresour Technol.*, 58, 217(1996).
doi:10.1016/S0960-8524(96)00113-7
- Bansal, R. C., Diksha Agarwal, Meenakshi Goyal, Krshna, B., Influence of carbon-oxygen surface groups on the adsorption of phenol by activated carbons, *Ind J. Chem. Tech.*, 9, 290-296(2002).
- Bansal, R. C., Donnet, J. B. and Stoeckli, F., Marcel Dekker, A review of: Active Carbon, Inc, New York, 482(1988).
- Chiou, M. S., Ho, P. Y., Li, H. Y., Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads, *Dyes Pigm.*, 60, 69(2004).
doi:10.1016/S0143-7208(03)00140-2
- Chou, K. S., Tsai, J. C., Lo, C. T., The adsorption of Congo red and vacuum pump oil by rice hull ash, *Bioresour Technol.*, 78, 217(2001).
Doi:10.1016/S0960-8524(00)00116-4
- Coughlin, M. F., Kinkle, B. K., Bishop, P. L., Degradation of azo dyes containing aminonaphthol by *Sphingomonas* sp strain 1CX, *J. Ind. Microbial Bio-Tech.*, 23, 341(1999).
- Elinge, C. M., Itodo, A.U., Peni, I. J., Birnin-Yauri, U. A., Mbongo, A. N., Assessment of heavy metals concentrations in bore-hole waters in Aliero community of Kebbi State, *Adv. Appl. Sci. Res.*, 2(4), 279-282(2011).
- Forgacs, E., Cserhati, T., Oros, G., Removal of synthetic dyes from wastewaters: a review, *Environ. Int.*, 30, 953-971(2004).
- Hirata, M., Kawasaki, N., Nakamura, T., Matsumoto, K., Kabayama, M., Tamura, T., Tanda, S., Adsorption of dyes onto Carbonaceous Materials Produced from Coffee Grounds by Microwave Treatment, *J. Colloid Interface , Sci.*, 254, 17-22(2002).
doi:10.1006/jcis.2002.8570
- Hesse, M., Meier, H. and Zeeh, B., Spectroscopic methods in organic chemistry, George Thieme, Stuttgart, Germany(1997).
- Indian Standard Institution, Activated Carbon, Powdered and Granular-Methods of sampling and its tests, Bureau of Indian Standards, New Delhi, IS 877(1989).
- Jambulingam, M., Karthikeyan, S., Sivakumar, P., Kiruthika, J., Maiyalagan, T., Characteristic studies of some activated carbon from agricultural waste, *J. Sci. Ind. Res.*, 66, 495(2007).
- Jia, Y. F., Xiao, B., Thomas, K. K., Adsorption of Metal Ions on Nitrogen Surface Functional Groups in Activated Carbons, *Langmuir.*, 18, 470-478(2002).

- Karthikeyan, S., Sivakumar, P. and Palanisamy, P. N., Novel Activated Carbons from Agricultural Wastes and their Characterization, *E-J. Chem.*, 5, 409-426(2008).
- Karthikeyan, S., Sivakumar, B. and Sivakumar, N., Film and pore diffusion modeling for adsorption of Reactive Red 2 from aqueous solution on to activated carbon prepared from bio-diesel industrial waste, *E-Journal of Chemistry*, 7(S1), 175-184(2010).
- Kishore K. Das, Bhanita Das, Bhupen K. Baruah. and Abani K. Misra, Development of New Probability Model with Application in Drinking Water Quality Data, *Adv. Appl. Sci. Res.*, 2 (4), 306-313(2011).
- Macias Garsia, A.,Valanzuela, C. and Gomez Serrano,V., Adsorption of Pb by heat treated and sulfurized activated carbon, *Carbon.*, 31, 1249-1255(1993).
[doi:10.1016/0008-6223\(93\)90083-M](https://doi.org/10.1016/0008-6223(93)90083-M)
- Manuel Fernando R Pereira, Samanta F Soaras, Jose, J. M. Orfao, Jose, L., Figueiredo, Adsorption of dyes on activated carbons: influence of surface chemical groups, *Carbon.*, 41(4), 811-821(2003).
[doi:10.1016/S0008-6223\(02\)00406-2](https://doi.org/10.1016/S0008-6223(02)00406-2)
- Namasivayam, C., Arasi, D. J. S. E., Removal of congo red from wastewater by adsorption onto waste red mud, *Chemosphere.*, 34, 401(1997).
[doi:10.1016/S0045-6535\(96\)00385-2](https://doi.org/10.1016/S0045-6535(96)00385-2)
- Namasivayam, C., Prabha, D., Kumutha, M., Removal of direct red and acid brilliant blue by adsorption on to banana pith, *Bioresour Technol.*, 64, 77(1998).
[doi:10.1016/S0960-8524\(97\)86722-3](https://doi.org/10.1016/S0960-8524(97)86722-3)
- Netpradit, S., Thiravetyan, P., Tow Prayoon, S., Application of 'waste' metal hydroxide sludge for adsorption of azo reactive dyes, *Water Res.*, 37, 763-772(2003).
[doi:10.1016/S0043-1354\(02\)00375-5](https://doi.org/10.1016/S0043-1354(02)00375-5)
- Rengaraj, S., Banumathi Arabindoo, Murugesan, V., Activated carbon from rubber seed and palm seed coats: Preparation and characterisation, *J. Sci. Ind. Res.*, 57, 129(1998).
- Renugadevi, N., Sangeetha, R. and Lalitha, P., Effectiveness of an economic adsorbent in the adsorption of methylene blue from an industrial dyeing effluent *Adv. Appl. Sci. Res.*, 2 (4), 629-641(2011).
- Robinson, T., Mc Mullan, G., Marchant, R., Nigam, P., Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Bioresour Technol.*, 77, 247-255(2001).
- Sharma, Y.C., Uma. and Upadhayay, S. N., Removal of cationic dye from water and water waste by adsorption on activated carbon developed from coconut coirs, *Energy and Fuels.*, 23, 2983-2988(2009).
[doi:10.1021/ef9001132](https://doi.org/10.1021/ef9001132)
- Summers, R. S., Roberts, P. V., Activated carbon adsorption of humic substances: I. Heterodisperse mixtures and desorption, *J. Colloid Interface Sci.*, 122(2), 367-381(1988).
[doi:10.1016/0021-9797\(88\)90372-4](https://doi.org/10.1016/0021-9797(88)90372-4)
- Sun, Y., Zhang, J. P., Yang, G. And Li, Z. H., Preparation of activated carbon with large specific surface area from reed black liquor, *Environ. Technol.*, 28, 491-497(2007).
[doi:10.1080/09593332808618810](https://doi.org/10.1080/09593332808618810)
- Way, L., Zhang, J. A., Zhao, R., Zharg, C. L., Li, C. and LI, Y., Adsorption of 2,4-dichlorophenol on Mn-modified activated carbon prepared from polygonum orientale Linn. *Desalination*, 266(1-3), 175-181(2011).
- Tripathi, P., Pinch Technology Reduces Wastewater, *Chem. Eng.*, 1996, 103, 87.